CHIRAL TAG ROTATIONAL SPECTROSCOPY FOR STRUCUTRE ANALYSIS OF CHIRAL METHYLPHENYL OXIRANE

HALEY N. SCOLATI, KEVIN J MAYER, MARTIN S. HOLDREN, BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*.

In chiral tagging, a smaller chiral molecule of known stereochemistry is non-covalently bonded, or "tagged" to the analyte of interest. This enantiomeric conversion results in a diastereomeric mixture of complexes whose stereochemistry can be spectroscopically resolved. In this work, rotational spectroscopy coupled with the chiral tag methodology was used to elucidate the multiple isomers produced by the analyte and tag motif of methylphenyl oxirane (MPO). The chosen tagging agent, 1,1,1-trifluoro-2-propanol (TFIP), has an energy difference of about 2 kJ/mol between its two possible monomer conformations. In this study, the 10 kcal/mol (42 kJ/mol) of internal energy available during the tag complex formation stabilizes the MPO/TFIP tag through non-covalent interactions, making it possible to observe the low energy isomers of the chiral complexes of both TFIP monomer conformations. The cooling of the TFIP monomer in the pulsed jet allows the population of the lowest energy conformer to be larger by at least a 10:1 ratio. As a result, the complexation energy can be viable tool in the exploration of the system's potential energy surface and conformational preference of the tag. Experimental data was collected on a 2-8 GHz CP-FTMW spectrometer, with additional 6-18 GHz measurements for the analysis of less abundant conformers. Additional tagging agents, such as propylene oxide (PO), were also screened. Candidate chiral tag complex structures were evaluated using DFT calculations (B3LYP GD3BJ / def2TZVP). From quantum chemical calculations, optimized geometry structures of the tag complexes can be assigned to the observed spectra. By combining these optimized geometries with known energy and dipole information, a high confident determination of the absolute configuration of MPO can be made. A survey of candidate structures as well as the experimental assessment of observed conformers will be discussed.